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## Thermal Conductivity of Semiconductors with Complex Crystal Structures

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### 6.1 Introduction

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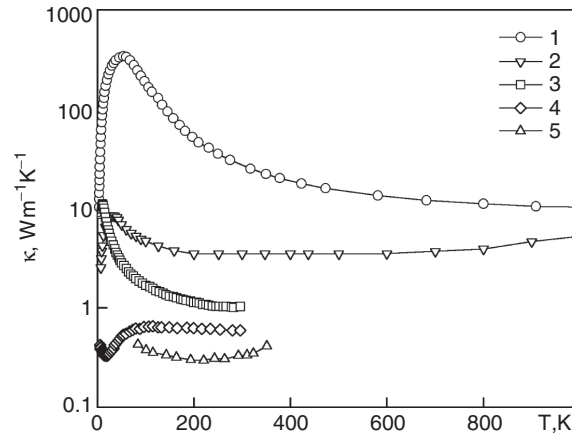
A number of crystals with many atoms in the unit cell show unusual dependence of the crystal lattice thermal conductivity ( $\lambda_L$ ) on temperature.<sup>1-4</sup> In this case, in the low-temperature region, the thermal conductivity of these crystals has a maximum and is atypical for crystals, which have a small number of atoms in the unit cell. In the high-temperature region, the lattice thermal conductivity depends weakly on temperature, and there is a wide plateau characteristic of amorphous solids. In [Figure 6.1](#) the temperature dependencies of  $\lambda_L$  are shown for a number of crystals having many atoms in the unit cell. Figure 6.1 shows that in some cases amorphous behavior of thermal conductivity in crystals having many atoms in the unit cell, or with very heavy unit cell, begins from very low temperature. The influence of the unit cell size on the lattice thermal conductivity can be studied more precisely when analyzing the temperature dependencies of  $\lambda_L$  in various modifications of boron and its crystal-chemical analogues, where rigid icosahedral structure takes place and the character of chemical bonding varies slightly.

### 6.2 Boron and Boron-Rich Borides

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[Figure 6.2](#) shows the temperature dependencies of the crystal lattice thermal conductivity for  $\beta$ -boron ( $\beta$ -B), amorphous boron, and a number of boron-rich borides. Their crystal lattice parameters are collected in [Table 6.1](#). Note the changes taking place in the temperature dependencies of  $\lambda_L$  when the number of atoms in the unit cell increases:

1. There is a strong dependence of the value and the character of temperature dependence of  $\lambda_L$  on the number of atoms in the unit cell.
2. The dependence of  $\lambda_L$  on temperature is different in the low-temperature and high-temperature regions for the crystals having large unit cells. For  $\beta$ -B and  $\alpha$ -AlB<sub>12</sub>, there is a wide plateau in the

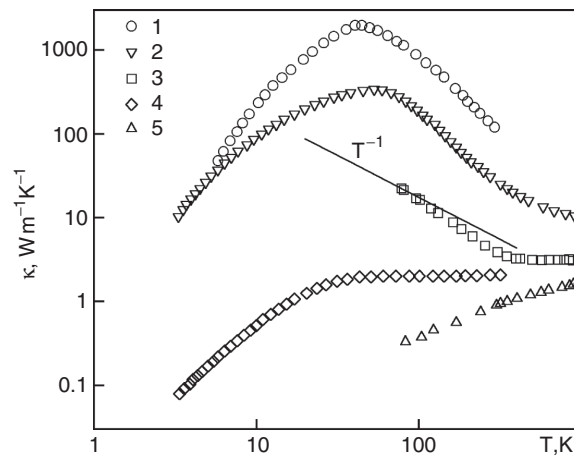


**FIGURE 6.1** Temperature dependencies of thermal conductivity of some materials with a complex crystal structure: 1,  $\beta$ -B<sup>1</sup>; 2,  $\text{MnSi}_{1.7}$ <sup>2</sup>; 3,  $\text{Cs}_8\text{Sn}_{44}$ <sup>3</sup>; 4,  $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$ <sup>3</sup>; 5,  $\text{Ag}_8\text{SnSe}_6$ .<sup>4</sup>

high-temperature region, whereas in the low-temperature region they exhibit a  $\lambda_L$  temperature dependence that is typical for crystals having a small unit cell.

3. In the temperature region from the maximum of  $\lambda_L$  up to the plateau, the  $\lambda_L$  decreases fast. For  $\beta$ -B in this region the value is  $\lambda_L \sim T^{-2}$ . To explain this feature in Ref. [7] a model was suggested that took into account the influence of crystal structure on the lattice thermal conductivity.

The model<sup>1</sup> considers separately contributions to the thermal conductivity from the low-frequency (acoustic) and high-frequency parts of the vibrational spectrum,  $\lambda_{ac}$  and  $\lambda_{hf}$  respectively. Acoustic phonons with wavelengths larger than twice the lattice period provide the dominant contribution to the thermal conductivity of  $\beta$ -B below 600 K. This conductivity component behaves in a way common for crystals exhibiting a maximum at low temperature. Since the unit cell manifests itself as a whole with respect to acoustic phonons, the specific heat associated with the acoustic branches should be, to a first approximation, inversely proportional to the number of atoms in the cell. Thus, in  $\beta$ -B it is about



**FIGURE 6.2** Lattice thermal conductivity of boron and some boron-rich borides: 1,  $\text{B}_{12}\text{As}_2$ <sup>5</sup>; 2,  $\beta$ -B<sup>1</sup>; 3,  $\alpha$ - $\text{AlB}_{12}$ <sup>6</sup>; 4,  $\text{YB}_{66}$ <sup>5</sup>; 5, amorphous B.<sup>7</sup> Solid line is the dependence  $\lambda_L \sim T^{-1}$ .

**TABLE 6.1** Crystal Structure Parameters of Boron and Boron-Rich Borides

Compound	Syngony	Structure Parameters, nm			Number of Atoms in Unit Cell	Reference
		<i>a</i>	<i>b</i>	<i>c</i>		
$\beta$ -B	Rhombohedral	1.0145		$\alpha = 65^\circ 17'$	105	8,9
$\alpha$ -AlB <sub>12</sub>	Tetragonal	1.016		1.426	187–208	9,10,11
B <sub>12</sub> As <sub>2</sub>	Rhombic	0.971	0.434	0.307	14	5
YB <sub>66</sub>	Cubic	2.344			402	12

one-hundredth of the value of that in a similar single-atom crystal. This does not manifest itself in the thermal conductivity of  $\beta$ -B at the lowest temperatures (in the region of the thermal conductivity maximum and lower temperature), where only long wavelength phonons are excited; whereas, it results in a strong decrease of  $\lambda$  at about room temperature and higher. It has been suggested that the high-frequency part of the spectrum provides a contribution  $\lambda_{\text{hf}}$  to the thermal conductivity, which is similar in magnitude and temperature behavior to the thermal conductivity of amorphous solids,  $\lambda_{\text{hf}}$  is dominant in the thermal conductivity of  $\beta$ -B at temperatures above 600 K.

It should be noted that the thermal conductivity  $\lambda_{\text{ac}}$  decreases in the series B<sub>12</sub>As<sub>2</sub>,  $\beta$ -B, and  $\alpha$ -AlB<sub>12</sub> approximately inversely proportional to the number of atoms in the unit cell of these materials. This allows the conclusion that the effective mean free path of acoustic phonons changes in this series by not more than a factor of 2 to 3 despite the fact that as one goes from B<sub>12</sub>As<sub>2</sub> to  $\alpha$ -AlB<sub>12</sub> the vibrational spectrum undergoes undoubtedly very large changes (the acoustic branches are cut off at ever smaller values of the wave vector while the number of “optical” phonons increases). B<sub>12</sub>As<sub>2</sub>,  $\beta$ -B, and  $\alpha$ -AlB<sub>12</sub> exhibit a sharp increase in the thermal conductivity with decreasing temperature. In all cases, the temperature dependence is stronger than  $\lambda \sim T^{-1}$ . For  $\beta$ -B, the temperature dependence is  $\lambda \sim T^{-P}$ , where  $P \geq 2$ . One of the reasons for such a strong temperature dependence may be the predominant scattering of acoustic phonons on optical ones.<sup>1</sup>

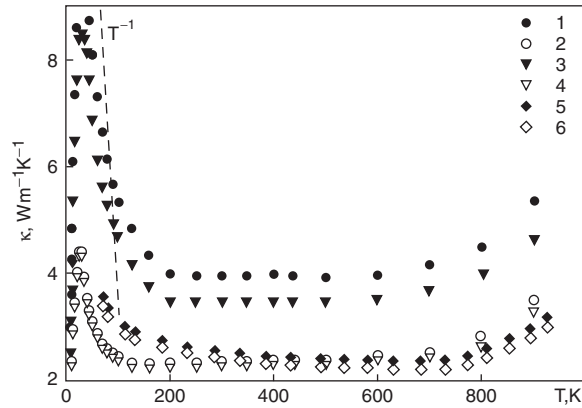
As the temperature increases,  $\lambda_{\text{ac}}$  decreases sharply while  $\lambda_{\text{hf}}$  increases. Therefore, at high temperatures  $\lambda_{\text{hf}}$  can become comparable with, or even exceed,  $\lambda_{\text{ac}}$ . The more complex the structure of a substance is, and hence, the smaller  $\lambda_{\text{ac}}$  is, the lower the temperature at which the contribution of  $\lambda_{\text{hf}}$  starts to become predominant. As a result, as one goes from B<sub>12</sub>As<sub>2</sub> to  $\alpha$ -AlB<sub>12</sub>, the thermal conductivity is expected to decrease and to approach in magnitude and temperature behavior that of amorphous boron. At the same time, the transition temperature from strong to weak temperature dependence should shift toward lower temperatures. Indeed, from Figure 6.2 it is seen that the more complex the structure of a substance, the more clearly pronounced becomes the region of amorphous thermal conductivity.

The two most structurally complex substances in the group studied,  $\alpha$ -AlB<sub>12</sub> and YB<sub>66</sub>, are very close to one another and to amorphous boron in the magnitude of their thermal conductivity at high temperatures; however, the atomic arrangement of YB<sub>66</sub> in the unit cell is very disordered while  $\alpha$ -AlB<sub>12</sub> has an ordered structure.

The authors believe that this allows two conclusions to be made. First, in substances with  $\alpha$ -AlB<sub>12</sub> or YB<sub>66</sub> structure, the contribution of acoustic phonons at high temperatures is very small. Secondly, in substances with a large number of atoms in the unit cell, the thermal conductivity at high temperatures is weakly sensitive to the arrangement of atoms in the cell. This supports the suggestion of Ref. [13] that the mean free path of high-frequency “phonons” does not exceed the size of the unit cell.

### 6.3 Higher Manganese Silicide

In the higher manganese silicide (HMS) case, the characteristic of boron and boron-rich borides features are seen more distinctly. In the region of where HMS exist, few commensurate crystal structures are described.<sup>2</sup> Even in the smallest unit cell of Mn<sub>4</sub>Si<sub>7</sub>, its length in the direction parallel to the C-axis is more than three times larger than that in the direction perpendicular to the C-axis. Large difference of the



**FIGURE 6.3** Temperature dependencies of thermal conductivity of HMS: 1, 2, 5 — total thermal conductivity; 3, 4, 6 — lattice thermal conductivity; 1, 3 —  $\parallel$ C; 2, 4 —  $\perp$ C; 5, 6 — pressed HMS. The dashed line is the dependence  $\lambda_L \sim T^{-1}$ .

sizes of the unit cell in these directions results in strong anisotropy of the crystal lattice thermal conductivity (Figure 6.3). As in the case of boron and boron-rich borides, here two regions can be outlined in the temperature dependence of the thermal conductivity. At  $T \leq 200$  K, one can see a classic temperature dependence determined by long-wave acoustic phonons with a maximum and a plateau due to the effect of optical phonons at higher temperature. The transition from the low temperature part of the dependence to the plateau takes place at a lower temperature for thermal flux directed along C-axis than that for the direction across C-axis due to large difference in the sizes of the unit cell.

In the low-temperature region between the maximum and plateau  $\lambda_L \sim T^{-P}$ . In the HMS case, unlike boron and boron-rich borides  $P < 1$ . This shows, that in this case, the optic phonons not only take part in the scattering of acoustic phonons, but also transport heat. Most probably because of the system of phase transitions in HMS, there is a softening in the number of optical phonon branches, and in this case the dispersion of these branches could be large enough. Essential contribution of optical phonons to the heat transport is confirmed by a relationship between thermal conductivity with the optical lattice vibrations damping in the solid solutions of HMS with  $\text{FeSi}_2$  analyzed in Ref. [14]. The increase of thermal conductivity at  $T > 800$  K is determined by bipolar diffusion of current carriers. Figure 6.3 shows that the strong disorder in a pressed sample results in the same effects as an increase in the unit cell length.

## 6.4 Argyrodites

$\text{Ag}_8\text{B}^{\text{IV}}\text{X}_6$  compounds (here  $\text{B}^{\text{IV}} = \text{Si, Ge, Sn}$ ;  $\text{X} = \text{S, Se, Te}$ ) belonging to the argyrodite family are very interesting subjects for a study of the influence of crystal structure features on lattice thermal conductivity because they have complex crystal structure and phase transitions with the symmetry change and doubling of the unit cell size. Figure 6.4 shows the temperature dependencies of lattice thermal conductivity for  $\text{Ag}_8\text{SnS}_6$ ,  $\text{Ag}_8\text{GeS}_6$ , and  $\text{Ag}_8\text{SnSe}_6$ .<sup>4</sup>

The high-temperature  $\gamma$  phases of each of these compounds had the fcc lattice with the constant  $a \approx 1.1$  nm; each unit cell contains four formula units ( $z = 4$ ).<sup>15,16</sup> Cooling of  $\text{Ag}_8\text{SnS}_6$  and  $\text{Ag}_8\text{GeS}_6$  caused a transition (at 445 and 496 K, respectively) to the  $\beta$  phase, which are also cubic, and this nearly doubled the lattice period to  $a \approx 2.1$  nm ( $z = 32$ ).<sup>16,17</sup> According to Refs. [16] and [17],  $\text{Ag}_8\text{SnSe}_6$  also exhibits one polymorphic transition at 356 K, forming the low-temperature  $\beta'$  phase, which is orthorhombic with parameters shown in the Table 6.2. In view of the complex crystal structure of the investigated substances, the temperature dependencies of their thermal conductivity should be similar to

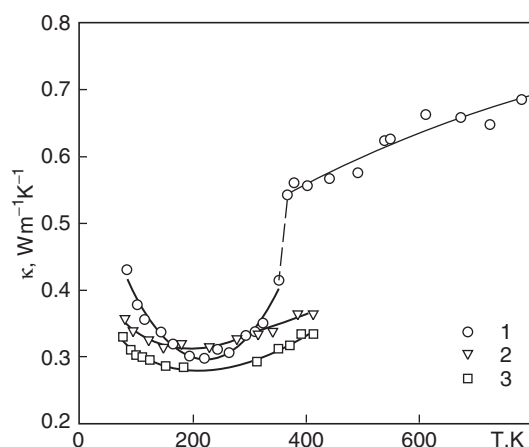


FIGURE 6.4 Thermal conductivity of the compounds  $\text{Ag}_8\text{B}^{\text{IV}}\text{X}_6$ , 1,  $\text{Ag}_8\text{SnSe}_6$ ; 2,  $\text{Ag}_8\text{SnS}_6$ ; 3,  $\text{Ag}_8\text{GeS}_6$ .<sup>4</sup>

those reported in Refs. [1,13] for  $\beta$ -B and for  $\alpha$ - $\text{AlB}_{12}$ , but the temperature of the transition from the crystalline to the amorphous nature of the thermal conductivity  $T_t$  should be quite different.

It follows from Figure 6.4 that above 120–140 K the lattice component  $\lambda_L$  weakly depends on temperature up to 300 K. At  $T > 300$  K, the temperature  $T_t$  could be estimated by equating the expression for the thermal conductivity of a monoatomic crystal with that of an amorphous substance.

The former expression could be the Leibfried–Schlomann equation,<sup>19,20</sup> in which the thermal conductivity should be reduced by a factor  $n$ , where  $n$  is the number of atoms in a unit cell;<sup>1,13</sup> the expression for the thermal conductivity of an amorphous substance could be taken in the form  $\lambda_a \approx (1/3) \cdot C_v \bar{v} \bar{l}^{21}$  and,<sup>22</sup> where  $C_v$  is the specific heat per unit volume;  $\bar{l} = \delta$  is the “mean free path” of elastic vibrations, assumed to be equal to the average interatomic distance  $\delta$ ;  $\bar{v}$  is the average velocity of sound.<sup>23</sup> In this way, one can obtain the following rough estimation of  $T_t$ :

$$T_t \approx 10^{-3} \frac{\Theta^2 \bar{A}^{5/3}}{n \gamma^2 \rho^{2/3}}$$

where  $\Theta$  is the Debye temperature,  $\bar{A}$  is the average atomic weight,  $\gamma$  is the Grüneisen constant, and  $\rho$  is the density.

Estimations of the transition temperatures of  $\beta$ -B and  $\alpha$ - $\text{AlB}_{12}$ , obtained from the equation gave  $T_t \approx 450$  K and  $\approx 250$  K, respectively (on the assumption that  $\gamma = 1$ ), which are close to those found experimentally. For the argyrodites under discussion,  $T_t \approx 50$ –80 K for  $n = 480$  was obtained ( $\Theta$  was estimated from the Lindemann equation<sup>24</sup> and was within the range 230–270 K).

TABLE 6.2 Crystal Structure Parameters of the Compounds  $\text{Ag}_8\text{B}^{\text{IV}}\text{X}_6$

Compound	Syngony	Space Group	Structure Parameters, nm			Number of Atoms in Unit Cell	Reference
			<i>a</i>	<i>b</i>	<i>c</i>		
$\gamma$ - $\text{Ag}_8\text{SnSe}_6$	Cubic (fcc)	$P4_332$	1.112			60	16
$\beta'$ - $\text{Ag}_8\text{SnSe}_6$	Orthorhombic	$\text{Pmn}2_1$	0.79168(6)	0.78219(6)	1.10453(8)	480	18
$\gamma$ - $\text{Ag}_8\text{SnS}_6$	Cubic (fcc)	$P4_332$	1.1			60	15,16
$\beta$ - $\text{Ag}_8\text{SnS}_6$	Cubic (fcc)		2.1			480	16,17
$\gamma$ - $\text{Ag}_8\text{GeS}_6$	Cubic (fcc)	$P4_332$	1.1			60	15,16
$\beta$ - $\text{Ag}_8\text{GeS}_6$	Cubic (fcc)		2.1			480	16,17

It is worth noting that the temperature dependence of  $\lambda$  and its value in the range  $T > 120\text{--}140\text{ K}$  are in full agreement with the above predictions for amorphous substances. The values of  $\lambda$  of the investigated crystals are  $\approx 0.3\text{ W K}^{-1}\text{m}^{-1}$ , which are considerably lower than the thermal conductivity of such a typical amorphous substance as fused quartz ( $1.3\text{ W K}^{-1}\text{m}^{-1}$  at room temperature) and three times lower than that of clathrates. Above  $356\text{ K}$ ,  $\text{Ag}_8\text{SnSe}_6$  exists in the  $\gamma$  phase, which has a structure simpler than the low-temperature phase. This transition is accompanied by an increase in  $\lambda$ , which is due to an increase of the contribution of the acoustic phonons to the thermal conductivity.

## 6.5 Conclusion

The characteristic features of the temperature dependence and absolute value of the thermal conductivity of some crystals having a large unit cell were explained on the assumption that amorphization (localization) of the high-frequency optical branch of the vibration spectrum occurred in the crystals. In this case, the lattice thermal conductivity can be regarded as composed of two parts. One of them is the contribution of the acoustic phonons to the thermal conductivity predominating at low temperatures and characterizing the material as a classic crystal. The other component is due to the optical branches of the vibrational spectrum, and it predominates at high temperatures and is amorphous, i.e., its absolute value is low and it is practically independent of temperature.

This fact shows that for the development of effective thermoelectrics it is necessary not only to optimize current carriers spectrum, but also the size and mass of a unit cell. In this case, it is possible to create a thermoelectric whose phonon system is similar to an amorphous one, and its electrical conductivity at optimum doping has a band character — contrary to amorphous solids.

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